

# NOTES

## *Determination of Residual Monomer in Polymer Emulsions by Extractive Distillation and Gas Chromatography*

The determination of residual monomer in polymer emulsions is important as an aid in the development of experimental conditions for polymerization and in the control of odor. Most methods for determination of residual monomers were not designed for polymer emulsions, but some could be adapted. Ultraviolet absorption,<sup>1</sup> mass spectrometry,<sup>2</sup> polarography,<sup>3</sup> and gel chromatography<sup>4</sup> have been reported. Some gas chromatographic methods for monomer in polymers involve dissolution of solid polymer in an appropriate solvent and direct injection of the solution,<sup>5,6</sup> precipitation of the polymer and injection of the supernatant,<sup>7</sup> and direct injection of polymer emulsion.<sup>8</sup> A sensitive gas chromatographic method using head-space analysis was reported by Steichen.<sup>9</sup> A method reported by this laboratory in 1963<sup>10</sup> separated ethyl acrylate from a polymer emulsion by distillation in the presence of toluene, which served the dual purpose of extractant and internal standard in the subsequent gas chromatographic determination.

The work reported herein describes a procedure for determining a variety of water-immiscible monomers in polymer emulsions. The method described is an improved and expanded version of that reported by Tweet and Miller,<sup>10</sup> which is applicable to a wider variety of monomers. The monomer is isolated from the emulsion by an extractive distillation in the presence of a measured amount of cyclohexane containing an internal standard. The method eliminates the problems connected with the direct injection of an aqueous polymer emulsion sample into the instrument and avoids the possibility of depolymerization of polymer in the injection port. It is also more sensitive than direct injection methods because the monomer can be concentrated in a much smaller volume.

### EXPERIMENTAL

**Apparatus.** Hewlett-Packard Models 5750 and 5880 gas chromatographs with flame ionization detectors were used for this work. Columns employed were a 6-ft  $\times$  0.25-in. glass, 0.1% SP-1000 on Carbowax C and a 6-ft  $\times$  0.25-in. glass, 5% Carbowax 20M on Anakrom ABS, 70/80 mesh. The distillation apparatus was described in the previous paper<sup>10</sup> and consisted of a 500-mL boiling flask, and 12.5-mL crankcase oil dilution type distilling receiver such as Corning No. 3582 and a condenser, all connected with 24/40 ground glass joints and assembled in the same manner as the well-known Dean-Stark apparatus for water.

**Reagents.** 3% (v/v) cyclohexanone in 99+% cyclohexane (Aldrich, Catalog no. 15,474-1) and 3% (v/v) *n*-octanol in 99+% cyclohexane; these are internal standard solutions and should be free of impurities which elute on the column in the region of the monomers of interest.

**Procedure.** A 50-g sample of emulsion is diluted with 125 mL of water in a 500-mL boiling flask. Known amounts of the monomers to be determined are weighed as standards into a second 500-mL boiling flask containing 175 mL of water. The monomer weights in the standard should approximate the expected weights of monomer in 50 g of sample. Exactly 3.00 mL of internal standard solution is pipetted into each flask and about 20 mg of hydroquinone, a few boiling chips, and two to three drops of antifoam are added. The apparatus is assembled, and the mixture is refluxed until the volume of organic layer in the receiver no longer increases (about 1.5 h). The upper layer is cooled, and a portion is pipetted into a vessel containing a few crystals of anhydrous sodium sulfate.

A 0.5- $\mu$ L sample of the organic layer is injected into the instrument, and the monomers are eluted at an attenuation which will produce reasonable-size, on-scale peaks. The peak areas of each monomer and the internal standard are measured, and the area ratios (monomer peak area/internal standard peak area) are calculated for each monomer.

$$\text{factor} = \frac{\text{g of monomer in standard}}{\text{area ratio of standard}}$$
$$\% \text{ monomer} = \frac{\text{factor} \times \text{area ratio of sample} \times 100}{\text{sample wt (g)}}$$

Alternatively, the amount of monomer can be obtained from a calibration curve of peak area ratio

TABLE I  
Monomer Recoveries<sup>a</sup>

Monomer	Amount added (g)	Amount found (g)	% recovery
Butyl acrylate	0.0157	0.0163	104
	0.0534	0.0536	100
Butyl methacrylate	0.0150	0.0152	101
	0.0576	0.0570	99
Ethyl acrylate	0.0190	0.0192	101
	0.0416	0.0427	103
2-Ethylhexyl acrylate	0.0177	0.0181	102
	0.0631	0.0597	95
Methyl methacrylate	0.0196	0.0190	98
	0.0573	0.0510	89
Styrene	0.0195	0.0196	101
	0.0558	0.0539	97

<sup>a</sup> The precision of the method was demonstrated with a series of 10 determinations on a polymer emulsion containing butyl acrylate, methyl methacrylate, and styrene. This sample was also analyzed using direct injection and the precision from 10 replicate analyses determined (butyl cellosolve was the internal standard in this case). Results are given in Table II.

vs. grams of monomer, but this is unnecessary since it has been shown that the calibration curve is a straight line in the range of interest.

## RESULTS AND DISCUSSION

This method has been applied to the determination of a variety of monomers including styrene, methyl methacrylate, butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, cyclohexyl methacrylate, and butyl methacrylate. Excellent resolution was obtained in all cases. The accuracy of the method was studied for butyl acrylate, butyl methacrylate, ethyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, and styrene by determining recoveries. Free monomers were removed from polymer emulsions by extraction and distillation with cyclohexane. Various levels of monomers were then added and the samples analyzed. Results shown in Table I show recoveries near 100%.

The method is applicable to monomers which can be steam-distilled and extracted into cyclohexane. This includes most water-insoluble monomers but excludes water-soluble or low-volatility monomers such as acrylic and methacrylic acids, hydroxyethyl methacrylate, vinyl pyrrolidone, dimethylaminoethyl methacrylate, and similar monomers. Monomers which are gases at room temperature, such as vinyl chloride, presumably would be lost through the condenser. Acrylonitrile is water-soluble, but the partition coefficient favors extraction into the organic layer so that it can be determined.

Some solvents and saturated impurities will interfere if they have the same retention time as a monomer of interest. Water-soluble solvents will not interfere unless the partition coefficients favor

TABLE II  
Precisions from Distillation and Direct Injection Methods<sup>a</sup>

Monomer	Distillation		Direct Injection	
	% Found	% Rel SD	% Found	% Rel SD
Butyl acrylate	0.0618	1.49	<sup>b</sup>	<sup>b</sup>
Methyl methacrylate	0.0171	1.16	0.0159	14.2
Styrene	0.0229	1.76	0.0205	34.7

<sup>a</sup> The poor reproducibility obtained using direct injection may be attributed to interferences from other components which prevent accurate measurement of the monomer peaks. Figures 1 and 2 are chromatograms obtained using direct injection and extractive distillation methods, respectively. The enhancement of the monomer peaks with respect to interferences is evident.

<sup>b</sup> Could not be determined due to interferences.

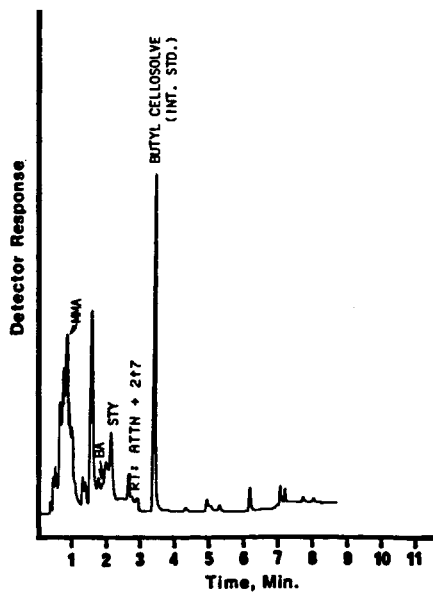


Fig. 1. Chromatogram of methyl methacrylate, butyl acrylate, and styrene in a polymer emulsion by direct injection.

extraction into cyclohexane. Ethylene glycol ethyl ether and diethylene glycol ethyl ether have been shown to remain in the water layer. Volatile saturated impurities derived from the monomers or initiator decomposition products can be determined simultaneously with the monomer. Butyl propionate, for example, a minor impurity in some lots of butyl acrylate, often is present in the

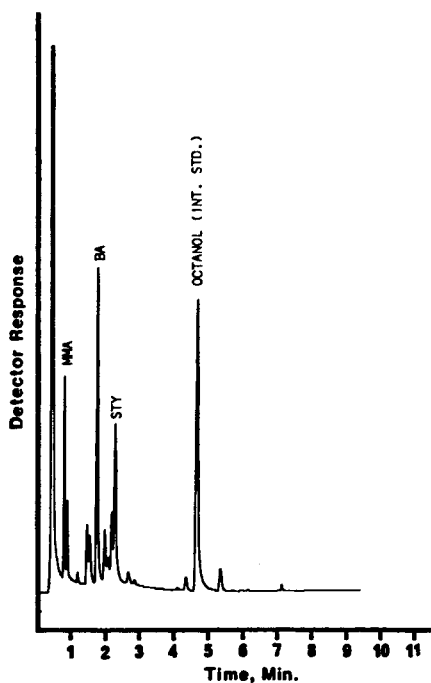


Fig. 2. Chromatogram of methyl methacrylate, butyl acrylate, and styrene in a polymer emulsion by extractive distillation with cyclohexane.

polymer emulsion at a level greater than that of the free monomer. This method can be extended to the determination of volatile, water-immiscible materials in samples other than emulsions.

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